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Tree coring as a complement to soil gas screening to locate PCE and TCE source zones and hot spots

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Abstract

Preliminary risk assessment for prioritisation of site investigations requires efficient screening to reveal type and level of contamination. The screening methods, tree coring and soil gas sampling were applied and compared at two forested sites contaminated with tetrachloroethylene (PCE) or trichloroethylene (TCE) to evaluate their ability to locate source zones and contaminant hot spots. One test site represented a relatively homogeneous sandy soil and aquifer, and the second a more heterogeneous geology with both sandy and less permeable clay till layers overlying a chalk aquifer. Tree cores from different tree species were sampled and analysed, and compared to soil gas measurements and existing soil gas data. Both methods were found useful as screening tools to locate hot spots of PCE and TCE in the shallow subsurface. Tree coring was found to be particularly beneficial as a complement to soil gas sampling at sites with low permeable soils, and where contamination was located in the capillary rise or shallow groundwater. The shorter time required for tree coring reduced the costs compared to soil gas sampling, but the sensitivity and precision of tree coring were lower. However, this did not affect the feasibility of using tree coring to locate the hot spots. Moreover, a combination of the two methods can help to focus any subsequent investigations like soil or groundwater sampling. The use of tree coring to complement soil gas sampling for pre-screening is expected to result in higher certainty for revealing hot spots and source zones at contaminated sites.

Keywords: phytoscreening, site investigations, plant uptake, wood, pore air, soil, groundwater, chlorinated solvents.

Introduction

The estimated number of potentially contaminated sites across Europe is 2.5 million, of which 1.17 million have been identified. 340,000 of these sites are expected to be contaminated and potentially require remediation (Liedekerke et al. 2014). This illustrates that many European sites are still in need of investigation. An internationally recognised standardised approach for site investigation has been developed (Lamé 2011). This approach involves three main steps: data collection, preliminary site investigation and detailed site investigation. Initially, data collection is carried out to provide factual knowledge about activities at the site, which may have been the source of groundwater or soil contamination (Danish EPA 2009; ICCS 2007). If the area is assessed as potentially contaminated, a preliminary site investigation follows. Subsequently, the acquired data on the occurrence and level of contamination used to determine if the contamination poses a risk for human health or for the environment (Overheu et al. 2014; Danish EPA 2009). If contamination above hazardous levels is detected, detailed site investigation and risk assessment follows, and options for site remediation and future use can be evaluated (ICCS 2007). Today, conventional investigation methods include quantitative analysis of groundwater and/or soil samples from drilling, direct-push and/or well installation (Döberl et al. 2012). The management costs of contaminated sites are high and the available resources are relatively limited compared to the large number of potentially contaminated sites. On average, only up to 15% of the total budget for contaminated sites in Europe is spent on site investigation and 81% on remediation (Liedekerke et al. 2014).

When chlorinated solvents like tetrachloroethylene (PCE) or trichloroethylene (TCE) are released and migrate into the subsurface, residual solvent phase (also known as non-aqueous phase liquid) remains. The solvent phase and sorbed phase contaminants constitute a continuing source of pollution and a risk of vapour intrusion and groundwater contamination. Therefore, finding the source zones has a high priority in site investigations, and rapid, efficient and economical preliminary screening methods are highly needed (Algreen et al. 2015; Döberl et al. 2012; Rein et al. 2011).

One well-established preliminary site investigation method is soil gas sampling (Rivett 1995; Bishop et al. 1990). Soil gas sampling is often used to evaluate the risk of vapour intrusion, but it can also be applied as a screening method for locating sources of volatile organic contaminants (VOCs) in the unsaturated zone (ICCS 2001). In some countries (e.g. Denmark), the use of soil gas sampling has been incorporated into the national guidelines for site investigations (ICCS 2007; 1999). Various standard practices for soil gas sampling have previously been published (ASTM international 2012; ICCS 1998). The feasibility of soil gas sampling is mainly dependent on the geological conditions and the properties of the contaminants. The method is useful in medium to high permeable unsaturated zones and for compounds with low boiling points, high Henry's law coefficients and low adsorption to the soil matrix (ICCS 1998), i.e. VOCs. However, soil gas sampling represents a relatively small capture zone, which is limited by the soil porosity and the pumped pore gas volume, Figure 1.

Phytoscreening has been suggested as a tool for the initial screening of large sites (Döberl et al. 2012; Algreen and Trapp 2014). Here, we test phytoscreening by tree core sampling, as a complimentary method to soil gas sampling for preliminary investigations of sites contaminated with chlorinated solvents. Phytoscreening is based on the fact that

contaminants such as TCE can be translocated from the root zone to the plant tissues above ground and subsequently sampled (Struckhoff et al. 2005; Orchard et al. 2000; Gopalakrishnan et al. 2007). With some limitations, the method can also be used to find BTEX (Algreen et al. 2015) and heavy metals (Algreen et al. 2012 and 2014; Stefanov et al. 2012; Wilson et al. 2013). Wood cores from trees are most frequently sampled because organic compounds accumulate in the wood (Trapp et al. 2001). Also, since trees have a large root system and thereby a large capture zone, the tree core will represent a large but relatively undefined soil volume, Figure 1. The roots can reach down to the upper groundwater and therefore may also reflect shallow groundwater contamination (Sorek et al. 2008; Vroblesky et al. 2004, Wittlingerova et al. 2013). The lateral extent of the root zone is generally reported to be 10-20 m in radius, but varies among species and with soil properties and climate (Stone and Kalisz 1991). The average maximum rooting depth in the temperate zone for a deciduous and a coniferous forest is approximately 2.9 m bgs and 3.9 m bgs, respectively (Canadell et al. 1996). Tree coring has been used to detect groundwater contamination in a sandy aquifer, where the water table was located as deep as 19 m bgs. (Sorek et al. 2008).

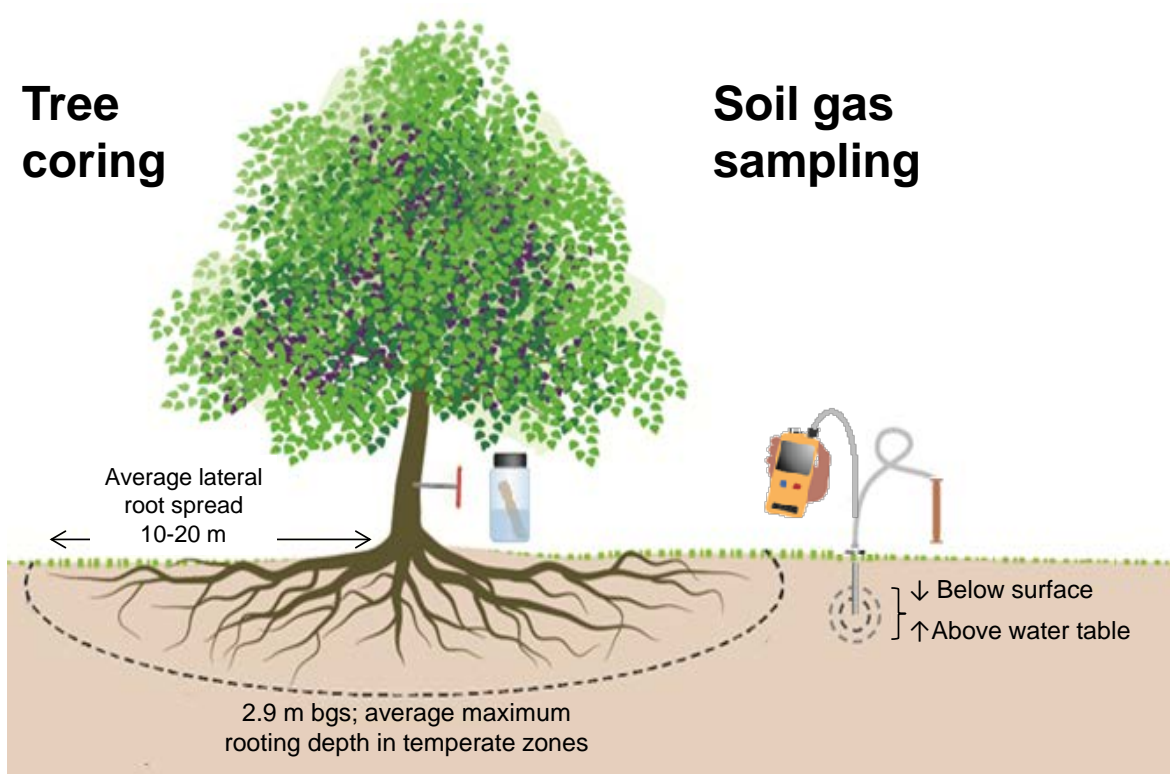


Figure 1: Conceptual model of tree coring and soil gas sampling including an indication of the capture zone of each method.

Tree coring was successfully applied to locate subsurface contamination by chlorinated solvents at many sites over the past decades (Limmer et al. 2011; Sorek 2008; Larsen et al. 2008; Vroblesky et al. 2004 and 1999). Tree coring has also been compared to other more advanced technologies, such as direct-push groundwater sampling (Rein et al. 2015) or direct-push based Membrane Interface Probing (MIP) (Larsen et al. 2008,

Algreen et al. 2015). In general, good agreement of results was found. Guidelines for phytoscreening have been established to increase the replicability and reliability of the results, but also with the intention to increase the dissemination of the method (Algreen and Trapp 2014; Trapp et al. 2012; Holm et al. 2011; Vroblesky 2008). However, commercial applications and acceptance of tree coring by authorities are still limited in many countries. Among the reasons for this may be the lack of knowledge of the application opportunities (pros and cons) and the fact that users are more familiar with the established soil gas sampling method.

The scope of this study was therefore to evaluate the feasibility and applicability of tree coring and soil gas sampling as preliminary screening methods for the location of contaminant source zones and hot spots. Both methods were compared at two forested sites contaminated mainly with PCE and TCE. The goals were to: i) compare results, applicability and limitations of tree coring and soil gas sampling as screening methods for PCE and TCE source areas and hot spots, ii) determine the sensitivity and the precision of the two methods, and iii) evaluate the costs associated with their application.

Test sites

Field sampling was performed at the two Danish test sites Platanvej and Grindsted.

At Platanvej, Falster, a furniture factory has used TCE for degreasing of metals in their production process over a 13-year period (1967-1980) until TCE was phased out. In 2006, soil and groundwater contamination with TCE above the Danish legal standards (5 mg/kg in soil, 1 µg/L in groundwater (Danish EPA 2014)) was encountered. This study was conducted in a forested area where soil gas investigations, including 26 sampling points (0.5-0.8 m bgs), in 2007 revealed a TCE hot spot with maximum soil gas concentrations up to 110 mg/m³ (DGE 2007). The soil gas data are given in Figure 2A. A closer look at the data reveals an elevated concentration area (maximum 1.4 mg/m³) south of the hot spot. Groundwater sampling of two wells placed in the vicinity of the hot spot (NW at SG21) and the elevated concentration area (SW at SG3) in the forested area showed TCE concentrations in µg/L (year of sampling) of: NW 5600 (2011) and 3100 (2012), and SW 700 (2007) and 880 (2012). The groundwater contaminant hot spot at SW was verified by multilevel sampling and monitoring (Ashur and Seibert 2015). Remedial groundwater pumping initiated in October 2009 approximately 100 m north of the forested area removed about 3 kg of chlorinated solvents annually. The removal has led to decreasing concentrations of TCE in the groundwater in the northern part of the forested area (Niras 2012). No further remediation has taken place at the test site. The site geology mainly consists of glacial deposits of quaternary sand down to about 3.5 m bgs, followed by clay till down to 4.0 m bgs, and tertiary chalk to the bottom of the boreholes (10-11 m bgs). The chalk consistency has an appearance similar to silty clay with a high content of limestone and flint. The primary groundwater aquifer is located in the chalk with the water table at approximately 3.4-4 m bgs (i.e. with the water table near the chalk-clay till interphase (DGE 2007)). The overall groundwater flow direction is east to southeast towards Guldborgsund (the sea). However, it is influenced by groundwater abstraction northwest and southeast of the site, and locally by the remedial pumping north of the forested area (Ashur and Seibert 2015).

In Grindsted, Jutland, a factory north-east of the study area has since 1914 used large amounts of chemicals, including chlorinated solvents, which has caused downstream groundwater contamination under an urban area toward the Grindsted Stream (Cowi 2011). An extensive investigation in 2010 of the potential vapour migration above the plume (vapour intrusion risk evaluation) revealed PCE contamination in the forested area from an unknown second source. This forested area was the focus of the current investigations. Samples from 14 soil gas sampling points (1.5 m bgs) collected in 2010 revealed PCE concentrations in the centre of the forested area of up to 3.21 mg/m³ (Cowi 2011). The soil gas data are given in Figure 2B. Groundwater sampling from three wells near (W317d and w316b) and down-gradient (W96) of the hotspot (for well locations see Figure 3) in 2010 showed PCE concentrations of 240, 510 and 52 µg/L, respectively. No remediation has been conducted at the Grindsted study area. Soil profiles show a sandy deposit down to 4 m bgs (Cowi 2011) consisting of quaternary glacial meltwater sand deposited as an outwash plain west of the Weichselian glaciation during the deglaciation period (Heron et al. 1998). It is underlain by tertiary micaceous sands with interbedded silt and clay 5-15 m bgs. The groundwater table is located 2.7 m bgs and the groundwater flow direction is south-west toward the nearby (<100 m) Grindsted Stream (COWI 2011).

Materials and Methods

Sampling

Two sampling campaigns were performed. During the first campaign, tree cores were collected from both Platanvej and Grindsted to investigate the feasibility of tree coring to locate the source areas and hot spots previously identified by soil gas sampling (Figure 2). A second campaign with simultaneous sampling of tree cores and soil gas took place in Grindsted to compare the methods without the sampling time lag and to test the precision of the methods. Also, groundwater samples from three existing groundwater wells were collected for further comparison. In both campaigns, tree cores from trees located within 3 m of the previous soil gas sampling points were collected. Tree species sampled were beech (*Fagus sylvatica*), oak (*Quercus robur*), pine (*Pinus sylvestris*) and maple (*Acer* sp.).

The first sampling campaign was performed on October 3rd and 4th, 2013. A total of 24 and 14 trees were sampled at Platanvej and Grindsted, respectively. The sampling procedure was carried out according to published guidelines (Algreen and Trapp 2014). In brief: two replicates were taken from each tree at a stem height of 1 m using a 6 mm increment borer (Suunto, Finland). The borer was drilled approximately 6 cm into the stem and the tree core extracted. The bark was discarded to avoid atmospheric influence and the remaining core was collected in analytical vials (20 ml) prepared with 4 ml water. Then, 0.5 ml internal standard (aqueous chloroform solution) was added and the vials were immediately closed to avoid volatilisation of compounds. The samples were protected against sunlight and cooled until chemical analysis to avoid degradation of the compounds. During sampling, the average outdoor temperature was 9-10°C, the average air pressure was 1020-1025 hPa (DMI 2014) and no precipitation occurred on the sampling day.

The second sampling campaign was performed in Grindsted on November 4th, 2014. Sampling was performed at three locations, which were selected based on the location of existing water wells. Sampling with each method was conducted within 3 m from each other, with the exception of sampling point 96/97 which was the closest available tree at a distance of approximately 10 m from the point of soil gas sampling and groundwater sampling. Tree cores were collected as in the first sampling campaign, but this time in triplicate around the circumference of each tree. Soil gas sampling was performed by use of an aluminium probe (6 mm in diameter) manually installed with a hammer into the subsurface soil after removal of the top soil by hand. Soil gas was collected in triplicate at each of the three depths: 0.5 m bgs, 1.0 m bgs and 1.5 m bgs (new probe installation for each sampling). Initially, the probes were purged with a syringe (V = 20 ml, 37 ml or 55 ml for the different depths (probe lengths), respectively). Afterwards, the PCE/TCE content in 420 ml soil gas was collected on ATD sampling tubes by the use of SKC-pumps. The tubes were packed with 100 mg Tenax, 40 mg glass wool and 100 mg Carbotrap. The flow was measured while sampling and never rose above 60 ml per minute. Samples were kept cool until later analysis. Groundwater samples were collected after the wells had been purged with a whale pump placed 1 m below the water table. The flow, oxygen concentration, pH, electrical conductivity, redox and temperature were monitored. After purging, the pump was placed just above the screen for sampling, and the flow was lowered if needed. Groundwater was sampled in 40 ml vials without headspace and conserved with sulphuric acid 4M. Samples were kept cool until later analysis. Seven additional tree core samples (from the same tree) and seven additional soil gas samples (new probe installation within a 1.5 m radius circle for each sample), i.e. 10 of each sample type in total, were collected at sampling point 317d (Figure 2) to test the precision of the methods.

During sampling, the average temperature was 9-11°C, the average air pressure 995 hPa (DMI 2014) and no precipitation occurred on the sampling day.

Chemical analysis

Tree core samples were analysed for PCE and TCE by HS-GC/MS (Headspace-Gas Chromatography/Mass Spectrometry) on an Agilent 7980 gas chromatograph system equipped with a Agilent 5975C electron impact (70 eV) triple-axis mass-selective detector. Samples were incubated on a rotary shaker at 250 rpm 85°C for 5 min. and 2 ml injected in split less mode at 80°C. Chromatographic separation was achieved on a 30 m x 0.32 mm I.D x 20.00 µm film thickness HP-PLOT/Q capillary column. The initial column temperature was set to 40°C for 4 min. then ramped at 35°C per. min to 290°C. The final temperature was held for 7 min and the total run time was 18.1 min, with Helium (1.6 ml per min) as the carrier gas. Measurements above the detection limit (DL) but below quantification limits (QL) were adjusted to half of the QL. DL's and QL's are given later in this section.

Soil gas was analysed for PCE by ATD-GC/MS (Automated Thermal Desorber- Gas Chromatography/Mass Spectrometry). The system consists of a Perkin-Elmer Turbomatrix with autosampler, an Agilent 6890 gas chromatograph and an Agilent 5973 Mass Selective Detector. Chromatographic separation is achieved on 30 m x 0.25 mm I.D x 20.00 µm film thickness Zebron ZB-624 capillary column. Operation parameters were;

column flow: 0.9 ml/min, system pressure: 6.9 psi, desorp flow: 30 ml/min., desorp time: 7 min., purge time: 1 min., trap hold: 5 min., total run time: 30 min., valves temp: 200°C, tube temp: 225°C, trap temp: 225°C, transfer line temp: 200°C. The temperature program started at 45°C for 3 min., and then the temperature increased at 15°C/min. until it reached 225°C, where it was then held for 2 min.

Groundwater was analysed by transferring 4 ml sample from the 40 ml sampling vials to 20 ml sealed analytical vials, containing 0.5 ml 4 % H₂SO₄ conservation and 0.5 ml internal standard (aqueous chloroform solution). The analytical procedure followed was the same as described for tree cores above.

Tree cores were analysed by the same method as water samples with the same standards/calibration curve, and the resulting concentrations are given as µg/L. One tree core sample contains 1 tree core whereas one water sample or standard contains 4 mL solution. Hence, a tree core concentration given as 1 µg/L is equivalent to 0.004 µg/tree core (or 4 ng/tree core). As tree core results are generally only reported as relative values the unit is of little relevance.

QL for tree cores were for the first campaign 0.70 µg PCE/L and 0.31 µg TCE/L. In the second campaign, the QL were 2.00 µg PCE/L for tree cores, 0.012 mg PCE/m³ soil gas, and 1.93 µg PCE/L groundwater.

Calculations of method precision

The precision was calculated for tree coring and soil gas sampling by the standard deviation based on ten samples from Grindsted (sampling point 317d, Figure 2). For the tree coring, the samples were collected evenly distributed around the tree circumference. For the soil gas, the samples were collected at 0.5 m bgs within a 1.5 m radius circle with a new probe installation for each sample. The ten samples were analysed in the same analytical sequence.

Cost estimation for the methods

The costs of each method were divided into: the cost of sampling including equipment (borer, pump etc.) and the cost of chemical analysis including material (chemicals, sampling vials etc.). The expense also includes payment of field personnel/laboratory technician and overhead costs. The expenses were estimated for both a single sample and for one day of sampling based on list prices from a Danish accredited commercial analytical laboratory and do not include travel expenses.

Results

Site investigations

Sampling was done within approximately three hours per site, and the chemical analyses were completed in one day. Screening results obtained by tree coring are shown by iso-concentration level contours, Figure 2. At Platanvej, tree coring identified the location of

two hot spots near sampling point 1 and 22, Figure 2C. In the area southwest of the two hot spots, TCE was not detected in the tree cores, though TCE was detected (but below the QL) in the former soil gas investigation (DGE 2007). At Grindsted, a hot spot identified in the centre of the study area in 2010 was confirmed by the tree coring, Figure 2D. North of the hot spot, PCE was not detected by tree coring, even though medium to low levels of PCE were detected by the previous soil gas sampling (Cowi 2011).

When the iso-concentration level contours based on tree coring are compared with the contours based on the previous soil gas sampling, strong agreement between the methods was found, Figure 2. Tree coring was able to locate all the hot spots located by soil gas sampling. Due to the different sampling matrixes (i.e. wood and soil gas), unequal capture zones and different years of sampling, some variation between the methods was expected and observed. Two noteworthy observations can be made. First, soil gas sampling seems to be more sensitive than tree coring because contamination was detected by pore air analysis in several points where it was not detected by tree core analysis. Secondly, at Platanvej two hot spots were clearly indicated by tree coring, the one to the north was also identified by soil gas sampling, whereas the one to the south had not been identified as a contaminant hot spot due to the relatively weak soil gas response, Figure 2A and 2C. The hot spot to the south may have been overlooked as a hot spot in the soil gas sampling due to the higher level measured in the northern hot spot during the soil gas sampling event conducted prior to remedial pumping.

A second sampling campaign at the test site Grindsted was carried out to obtain data by tree coring and soil gas sampling at the same time for a better comparison. In addition groundwater samples were collected. The measured PCE concentrations were normalised (where 100% represents the maximum concentration obtained by each method and depth for soil gas sampling) and shown in Figure 3. High concentrations were measured by both tree coring and soil gas sampling in the centre of the forested area, near sampling point 317d. The concentrations in soil gas at sampling point 317d and 316b were very similar. However, at point 316b the concentration measured by tree core sampling was relatively low. At point 96/97 both tree core and soil gas concentrations were low. No direct relation was found to the groundwater concentrations, which were relatively similar and appeared to increase towards south/southwest (in the direction of flow, towards Grindsted Stream).

By comparing the results from the first sampling campaign (Figure 2B and 2D) with results from the second sampling campaign (Figure 3), it is observed that the same hot spot was located in both campaigns, even though different concentrations were measured.

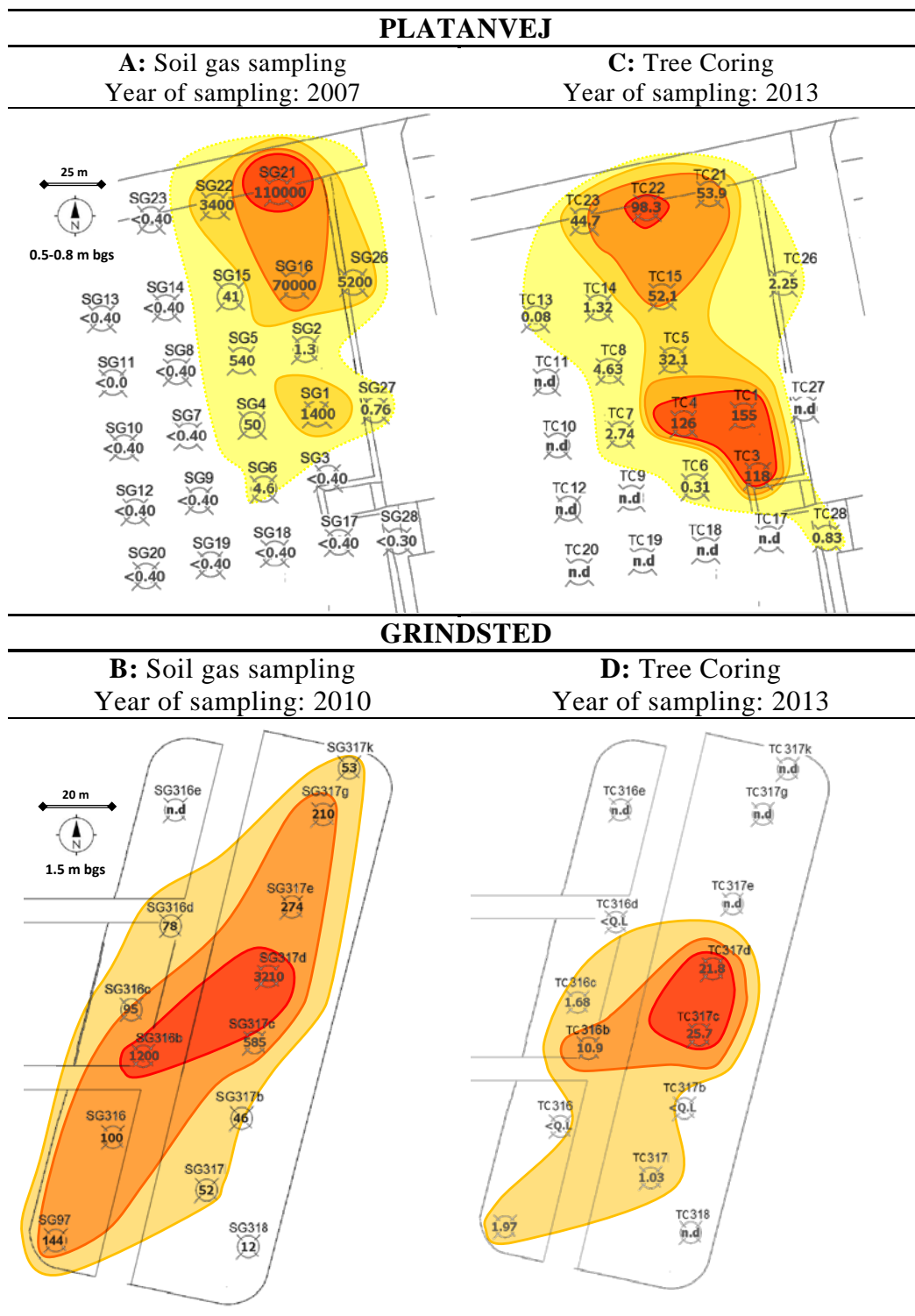


Figure 2: Site maps showing sampling points and iso-concentration level contours of TCE (Platanvej) or PCE (Grindsted) obtained by tree coring ($\mu\text{g/L}$) and soil gas sampling ($\mu\text{g/m}^3$) (Cowi 2011, DGE 2007). Darkest colour indicates highest measured concentration level and lightest colour lowest detectable concentration. Bold numbers indicates measured concentrations where n.d = not detected ($<\text{D.L.}$), $<\text{Q.L.}$ = detected but below quantification limit.

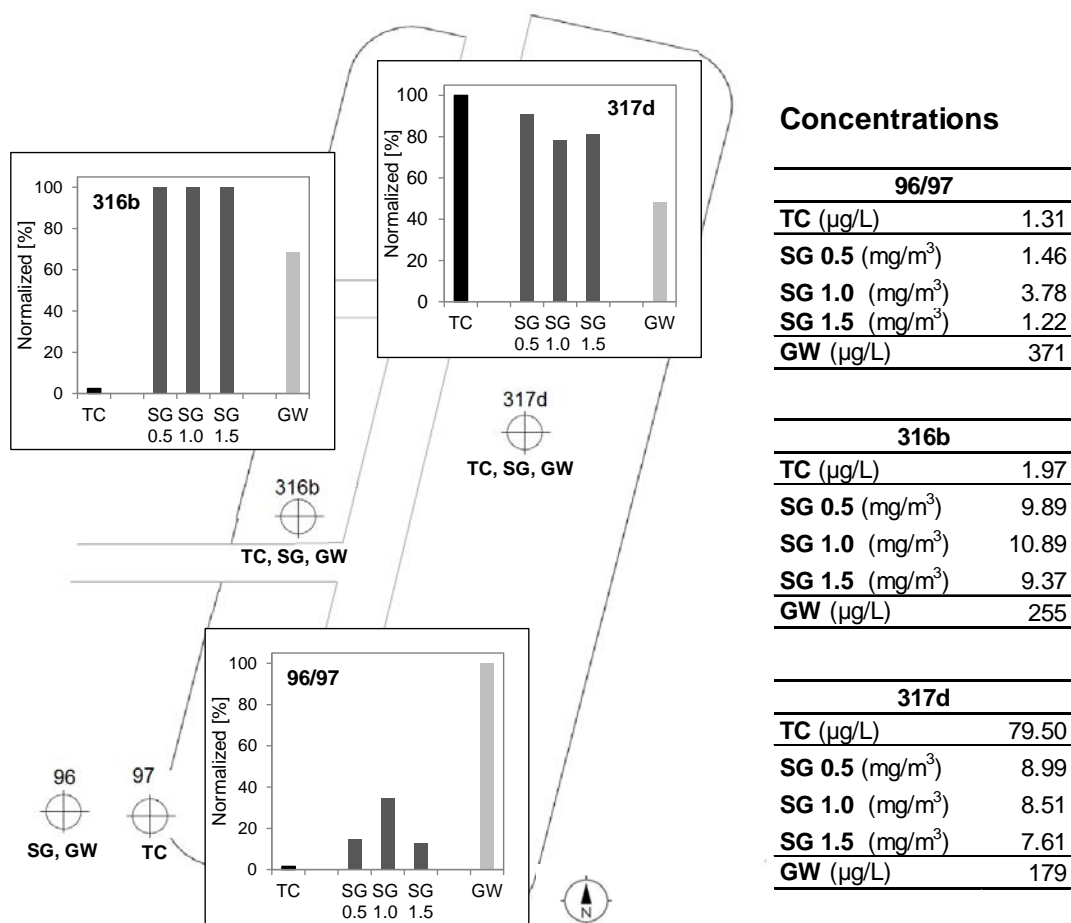


Figure 3: Normalised PCE concentrations obtained during the second sampling campaign at Grindsted, where 100% represents the maximum concentration obtained by each method and depth for soil gas sampling. Sampling was done simultaneous by tree coring (TC), soil gas sampling (SG) (SG at three depths, 0.5, 1.0 and 1.5 m bgs) and groundwater sampling (GW). Numbers in the figures represent the sample point ID seen on the plan in background and in Figure 2.

In addition, soil gas was sampled at three different depths to investigate whether tree coring is more representative of conditions near the ground surface or deeper in the subsurface, e.g. near the groundwater table. The results are inconclusive because the concentrations measured at the three depths were very similar in the relatively homogeneous sandy deposit.

The precision of tree coring and soil gas sampling

The precision of tree coring was calculated based on ten replicates sampled around the circumference of one tree. The measured concentrations were between 20.4 $\mu\text{g/L}$ and 155 $\mu\text{g/L}$ (mean; 79.5 $\mu\text{g/L}$), giving a relative percent difference (RPD) of 52 %. For soil gas sampling, taken at 0.5 m bgs within 1.5 m in radius with a new probe installation for each

sample, the measured concentrations ranged from 7.90 mg/m³ to 10.1 mg/m³ (mean; 8.99 mg/m³) which gives a RPD of 8 %.

Application costs of tree coring and soil gas sampling

An estimation of the costs for application of tree coring and soil gas sampling are given in table 1. The costs will depend on the number of samples due to fixed “start-up” expenses. The cost based on a single sample is approximately 64 € and 142 € for tree coring and soil gas sampling, respectively. This makes the price of soil gas sampling almost twice that of tree coring. Based on one day of site screening, the costs are similar; however the number of samples obtainable differs. The cost of soil gas sampling is approximately 2100 € per day and yields 15 sampling points, where the cost of tree coring is approximately 1800 € per day and includes sampling of 40 trees.

Table 1: Overview of round off prices for soil gas sampling and tree coring (€).

Method		Sampling cost	Analysis cost	Total
Tree coring	1 single sample	18	46	64
Soil gas sampling		91	51	142
Tree coring, 40 sampling points	1 day of sampling	540	1290	1830
Soil gas sampling, 15 sampling points		1370	765	2135

Discussion

Opportunities of application

Both tree coring and soil gas sampling have advantages and limitations which should be taken into account along with the purpose of the site investigation when selecting the preliminary screening method. The pros and cons of the two methods in the context of finding contaminant source zones and hot spot areas are listed in Table 2. In general, tree coring is a fast, simple and mobile (hand drill) method favourable at large sites (Algreen et al. 2015) or at sites with problematic subsurface, e.g. buried installations or hazards such as cables or explosives, because no interruption of the subsurface is needed (Trapp et al. 2012). Obviously, tree coring will be limited by the location of trees. Soil gas sampling is well suited at smaller sites. Due to the relatively small and more defined capture zone, the method can be applied in a more discretised grid (both horizontally and vertically). Both methods are semi-quantitative and affected by changes/variations in conditions: Soil gas to infiltration of precipitation and to barometric pressure changes, tree coring to evapotranspiration (temperature and season) and both likely to groundwater level fluctuations. Relatively rapid changes due to infiltration and pressure changes will to a higher degree affect the results of soil gas sampling (Mills et al. 2007; Wyatt et al. 1995) compared to tree core sampling, because trees can accumulate contaminants such as PCE and TCE in the wood over several weeks (Wittlingerova et al. 2013; Trapp 2007). Though the concentrations were not reproducible, the study showed that location of the hot spots was feasible with tree coring.

Table 2: Overview and comparison of the tree coring (TC) and soil gas sampling (SG) methods for site pre-screening to locate source areas and contaminant hot spots with chlorinated solvents. +++ indicates very useful/beneficial. – indicates not useful/challenging.

		Tree coring	Soil gas sampling	Comments
Application	Useful at large sites e.g. brownfield	+++	++	TC is faster, more mobile and by default has a larger capture zone than SG
	Useful at small sites	+	+++	SG can be applied in more discretised grid (both horizontally and vertically)
	Sensitivity to the soil properties	++	-	TC can be applied everywhere where trees are growing, as long as contamination is not too deep. SG cannot be applied in low permeable soils and in the capillary or saturated zone.
	Restrictions of sampling	++	++	Installing the SG probe can be difficult depending on the soil structure e.g. stones, rocks or hard soil blocking the probe. For TC trees need to be present and the method is not useful indoors.
	Impact on the environment/ surroundings	+++	+++	Only small hand-held equipment is needed for sampling. Sampling only leaves small holes in trees or soil, respectively
	Sensitivity of the method	+	++	Lower sensitivity of TC may be due to dilution of the contaminants (roots integrate over large capture zone), degradation of the contaminants in the root zone/planta or volatilisation of the contaminants from the plant tissue above ground
	Spatial resolution of the method	+	++	The size of the soil area and the sampling depth can be adjusted during SG
	Mobility of the method	+++	++	Less equipment is needed for TC
	Applicability at problematic underground structures	+++	+	Shallow pipes and cables and other underground structures may limit accessibility for SG, but not for TC
Sample / Analysis	Representation of large soil volumes	+++	++	TC usually represents a larger soil volume, SG (depending on the geology) usually smaller areas of contamination
	Identification of the area represented by sampling	+	+++	The area SG represents depends on the soil porosity and volume extracted, but is more specific/discrete than TC. Small hot spots may be overlooked by tree coring due to the dilution effect of the large capture zone.
	Data treatment and interpretation	++	+++	The data treatment is identical for SG and TC
	Level of detail	+	++	SG can give information in the vertical direction
	Potential of false Negatives	- -	-	It can happen that the contaminants in soil or groundwater are not accessible for plant uptake or soil gas collection
Costs	Sampling	+++	++	Tree coring can be done more rapidly
	Analysis	++	++	Similar

Practicability of application

Some major differences between tree coring and soil gas sampling such as the size of the capture zone, the sensitivity, the precision and the impact of the geologic and hydrogeologic conditions were observed in this study. The capture zone of tree coring is much larger than that of soil gas sampling due to the widespread root system, illustrated in Figure 1. At Grindsted, a relation was found between the concentrations in tree cores and soil gas, whereas no direct relation between the concentrations in tree cores (or soil

gas) and groundwater was found based on the three groundwater sampling points. This indicates that PCE in tree cores from the Grindsted test site are mostly related to the presence of PCE in the unsaturated zone, similar to soil gas sampling.

A different observation was made at Platanvej. Here, tree cores at both contaminant hot spots (NW and SW) clearly revealed strong contamination in the subsurface (confirmed by groundwater sampling). The hot spot in SW was only weakly reflected in the soil gas. An explanation for this is the trees' ability to take up contaminants from both groundwater, capillary zone pore water and soil gas (Struckhoff et al. 2005). Except in dry seasons, trees take up most water from the upper soil. Uptake from groundwater occurs when the overlying soil is depleted in water, which is often the case in dry periods (Smith et al. 1997; Dawson and Pate 1996). At Platanvej the water table is located below a clay till layer separating unsaturated sand and the chalk aquifer. The finding is in accordance with previous studies, where relations between concentrations in wood and in shallow groundwater were found (Larsen et al. 2008; Gopalakrishnan et al. 2007; Wittlingerova et al. 2013). This shows that tree core sampling may also be of use to locate chlorinated solvents in shallow groundwater. Soil gas sampling is challenged by low permeable soil layers and is limited to the unsaturated zone. This can be critical to the use of the method as seen in this study for Platanvej, where a low permeable soil layer above the water table is present. This layer inhibits the upward migration of TCE contaminants in the unsaturated zone and may limit or prevent detection of the underlying groundwater contamination by soil gas sampling. In such cases, tree core sampling can complement the screening efforts, because tree roots are able to penetrate low permeable soil layers (Vroblesky et al. 2004; Canadell et al. 1996), and thereby allow contaminant translocation from and below the low permeable layer.

The extremely high soil gas concentrations observed in the NW hot spot at Platanvej, were not reflected to the same extent in the tree cores. This is mainly due to the remedial groundwater pumping initiated in 2009 approximately 100 m north of the hot spot (soil gas sampling took place in 2007 before the remedial pumping, and tree coring in 2013). About 3 kg of chlorinated solvents have been removed annually (Niras 2012), causing decreasing concentrations in this hot spot.

This study showed that tree coring has a lower sensitivity and precision than soil gas sampling. This may be due to: (1) dilution of the contaminants as the tree's capture zone is much larger than that of soil gas sampling, see Figure 1, (2) degradation of the contaminants in the root zone and in plants (Shang et al. 2001; Newman et al. 1999), or (3) volatilisation of the contaminants from the plant tissue above ground (Burken and Schnoor 1998, 1999). However, with the greater coverage potential obtainable at low cost by tree coring, the lower sensitivity and precision might well be a small trade off.

A more sensitive analytical method than HS-GS/MS for tree cores could be SPME-GS/MS. Other sampling technologies such as in plant SPME or passive sampling devices (Limmer et al. 2011, 2014a and 2014b; Shetty et al. 2013; Sheehan et al. 2012) can enhance the sensitivity and also enable monitoring of the same tree over long periods.

The low precision in replicate sampling is also due to the fact that the tree cores are taken from different locations around the circumference of the stem; each location is connected via xylem to a specific part of the root system and therefore the replicates represent different parts of the subsurface (Limmer et al. 2013; Holm and Rotard 2011). In

addition, small variations among the replicates are related to inhomogeneity of the wood samples, such as different tree core lengths and different water and lignin content of the wood. Larsen et al. (2008) suggested that the precision could be optimized by taking into account the sample mass and the water content of the tree core sample. However, the variation in concentrations within the trees uptake zone is typically much larger than the variation in tree core weight and water content.

Conclusions

This study has clearly shown that tree coring can be a useful screening tool for contamination in unsaturated zones but also in shallow saturated zones. Both sensitivity and precision were lower for tree coring than for soil gas sampling, based on 10 replicates taken at the same sampling point. Nonetheless, all known hot spots were identified. The use of tree coring is more cost efficient than soil gas sampling due to fast field sampling (40 samples per day versus 15/d) and because a larger soil volume is investigated by each tree core sample than by each soil gas sample. The combination of both techniques for screening of contaminated sites for the presence and location of source zones or hot spots is therefore expected to lead to a more reliable result.

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